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Coordination Structure of Cu^{2+} Ion in Highly Concentrated Aqueous $CuBr_2$ Solution, Determined by X-Ray Diffraction Analysis

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The solute structure of concentrated aqueous copper(II) bromide solutions was determined by the analysis of the radial distribution curves of X-ray diffraction measured on the solutions with varying concentrations, 4.364—1.016 mol dm^{-3}. The mixed-ligand aquabromocopper(II) complexes were found to be present in these solutions, and to have a distorted octahedral geometry. The Cu^{2+} ion was coordinated with Br^- ions at the equatorial sites whose bond lengths were shorter than the axial sites. The interatomic distances of the equatorial Cu–Br and Cu–OH_2 bonds were, respectively, 2.42—2.46 and 1.96—1.99 Å, and that of the axial Cu–OH_2 bond, 2.37—2.51 Å. The average coordination number of Br^- ions in the nearest neighbor of the Cu^{2+} ion increased from 0.33 to 1.31 as the concentration of $CuBr_2$ increased from 1.016 to 4.364 mol dm^{-3}. Even in the 4.364 mol dm^{-3} solution, which was nearly saturated, the coordination of the Br^- ion at the axial site was not evidenced. In the 1.474 mol dm^{-3} $CuBr_2$ solution dissolved in an aqueous 6.923 mol dm^{-3} HBr solution, the tetrabromocopper(II) complex species was proposed to exist in a flattened tetrahedral form, wherein the Cu–Br distance was 2.41 Å.

The octahedral structure of six-coordinate copper(II) complexes has been characterized by two kinds of coordination bonds, with different bond lengths, *i.e.*, a shorter one toward the equatorial site and a longer one toward the axial site; this has been interpreted as being related to the anisotropic electron-filling on the dγ orbitals of Cu^{2+} ion in the octahedral ligand-field. The X-ray investigations have demonstrated that the mixed-ligand complexes $[Cu(en)_2(H_2O)_2]^{2+}$ and $[Cu(NH_3)_4(H_2O)_2]^{2+}$ in the aqueous solution have a structure wherein the two H_2O molecules are coordinated at the elongated axial sites, with a Cu–O bond distance of 2.92 Å in the former and of 2.33 Å in the latter.[1,2] On the other hand, Wertz *et al.* have determined the solute structure and the average coordination number around the Cu^{2+} ion with the concentrated aqueous $CuCl_2$ solutions of 3.18 and 4.35 mol dm^{-3}, and they have concluded that the coordination ability of the Cl^- ligand is $Cl^- \ggg H_2O$ toward the axial coordination and $Cl^- > H_2O$ toward the equatorial coordination.[3,4] Judging from the spectrochemical series, Cl^- is expected to exert a weaker ligand-field than H_2O upon Cu^{2+}. The X-ray investigation by Golik *et al.* has shown that in the predominant complex species which are present in the aqueous 2.0 mol dm^{-3} $CuCl_2$ solution, two Cl^- ions are coordinated axially and four H_2O molecules are coordinated equatorially with Cu^{2+}.[5,6] From the UV- and visible-spectral investigations, Libuś has also supported the axial coordination of the Cl^- ligand in the complex $[CuCl(H_2O)_5]^+$ existing in the aqueous $CuCl_2$ solution.[7]

In contrast to the above results, Fontana *et al.* have reported the Raman spectrum of the aqueous 3.4 mol dm^{-3} $CuCl_2$ solution; it shows a pattern similar to that of crystal $(CH_3NH_3)_2CuCl_4$, which is composed of square-planar complex $[CuCl_4]^{2-}$.[8] Moreover, as for the aqueous 0.5 mol dm^{-3} $CuBr_2$ solution, the EXAFS measured by Fontaine *et al.* indicated that in the solution half of both the Cu^{2+} and the Br^- ions are linked each other with an interatomic distance of 2.35 ± 0.05 Å; this distance is rather closer to the equatorial Cu–Br than to the axial Cu–Br bond distances in crystal $CuBr_2$.[9–11] Hence, it is of interest to determine by X-ray investigation whether the coordination of the Br^- ion in the mixed-ligand aquabromocopper(II) complexes occurs at either the axial or the equatorial sites. Previously, we have reported that the X-ray scattering factor of the bromine is larger than that of the chlorine atom. This caused pronounced peak appearance in the X-ray radial distribution curve, which rendered a precise resolution of the solute structure of the aqueous $NiBr_2$ solution.[12] In the present paper, we attempt to elucidate the coordination structure of the mixed-ligand aquabromocopper(II) complexes in the aqueous solution by the X-ray investigation.

Experimental

Sample Solutions. The sample solutions A—D were prepared by dissolving copper(II) bromide obtained by the recrystallization of commercially available material from distilled water. The sample solutions E and F were prepared by dissolving recrystallized copper(II) bromide in an aqueous 47% hydrobromic acid solution, and then by diluting the solutions with distilled water. The copper and bromide ion concentrations of the solutions were determined by EDTA titration and the Volhard method, respectively. The composition of the sample solutions is shown in Table 1.

X-Ray Diffraction Measurements and Data Treatments. After the sample solutions had been left to stand at room temperature for 2—3 d, the diffraction intensities of the solutions were recorded, as previously reported.[12] The scatterd intensities were measured at every 0.1° between $\theta=0.5°$ and 8°, 0.25° between $\theta=8°$ and 30°, and 0.5° between $\theta=30°$ and 65°; 2θ is the scattering angle. The time required for accumulating 40000 counts was recorded for the solutions A, B, C, E, and F; 80000 counts were taken for the solution D.

The measured intensity data were corrected for the air- and multiple-scatterings, and for the polarization and absorption due to the sample solutions, and then normalized to absolute intensities $I(\theta)$ according to the ordinary treatment.[13,14] Reduced intensities $i(\theta)$ were calculated by subtracting incoherent and independent coherent scatterings from $I(\theta)$.

The radial distribution function $D(r)$ employed is given in in Eq. 1:

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TABLE 1. COMPOSITION AND PARAMETER VALUES OF SAMPLE SOLUTIONS

	Solution					
	A	B	C	D	E*	F*
Cu(mol dm^{-3})	1.016	2.006	3.262	4.364	2.101	1.474
Br (mol dm^{-3})	2.032	4.011	6.524	8.728	8.345	9.871
O (mol dm^{-3})	53.96	51.40	48.62	47.33	44.50	38.98
H (mol dm^{-3})	107.4	102.8	97.25	94.66	93.13	84.89
[Br]/[Cu]	2.00	2.00	2.00	2.00	3.97	6.70
V/Å^3	1634	827.7	509.0	380.5	790.3	1127
ρ/g cm^{-3}	1.199	1.374	1.605	1.827	1.606	1.592
μ/cm^{-1}	17.41	33.18	53.20	70.80	60.97	68.56

V, Stoichiometric volume containing one copper atom. This is used for diffraction data normalization; ρ, density; μ, linear absorption coefficient of the solution; *, hydrobromic acid solution.

$$D(r) = 4\pi r^2\rho_0 + \frac{2r}{\pi}\int_0^{15} s\cdot i(s)\cdot M(s)\cdot\sin(r\cdot s)\cdot ds, \qquad (1)$$

where ρ_0 is the average scattering density of the sample solution, and is given in the electron units, and s is equal to $4\pi\sin\theta/\lambda$ (λ=0.7107 Å). The modification function $M(s)$ was that employed previously.[12]

As a first approximation to the structure, the theoretical peak shape was drawn by Fourier transformation of the theoretical intensities $i(s)_{\text{calcd}}$ given by Eq. 2:

$$i(s)_{\text{calcd}} = \sum_i^{i\neq j}\sum_j n_{ij}\cdot f_i(s)\cdot f_j(s)\,\frac{\sin(r_{ij}\cdot s)}{r_{ij}\cdot s}\exp(-b_{ij}\cdot s^2). \qquad (2)$$

In Eq. 2, f_i(s) and f_j(s) are the atomic scattering factors of atoms i and j; and n_{ij}, r_{ij}, and b_{ij} are, respectively, the frequency factor, the distance and the temperature factor of the interactions between atom i and j.

In order to attain more precisely the structural parameter values, the above parameter values were refined so as to minimize the difference between $i(s)_{\text{calcd}}$ and observed $i(s)$, by means of a least-squares refinement.

Results

The radial distribution curves $D(r)$ and $D(r)-4\pi r^2\rho_0$ are shown in Figs. 1 and 2. For the solutions A—D, four peaks are seen in the $D(r)$ curves at *ca.* 1.0, 2.0, 2.5, and 3.3—3.5 Å; these would be closely concerned with the intra- and inter-molecular atomic interactions of the solute complex and the solvent H_2O molecules. The first broad peak around 1.0 Å is caused by the O–H interaction within the free and complexed H_2O molecules in the solution. The peak ascribable to these O–H interactions has been commonly observed in the $D(r)$ curves measured for the aqueous solution.[12,15]

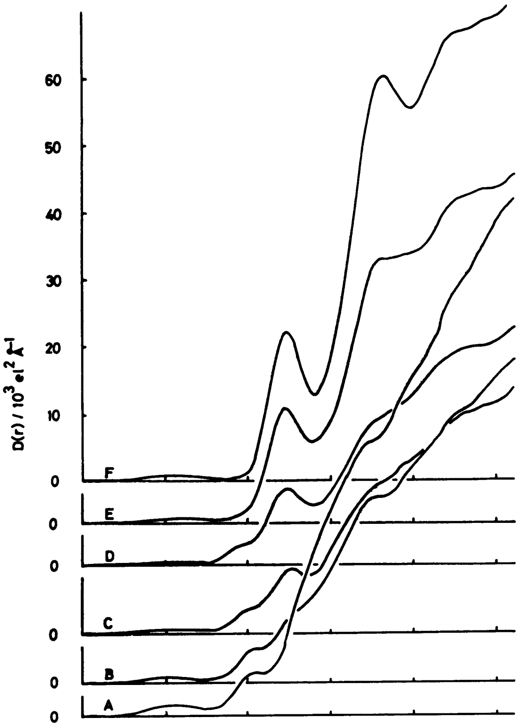

Fig. 1. Radial distribution curves $D(r)$ for the solutions A—F.

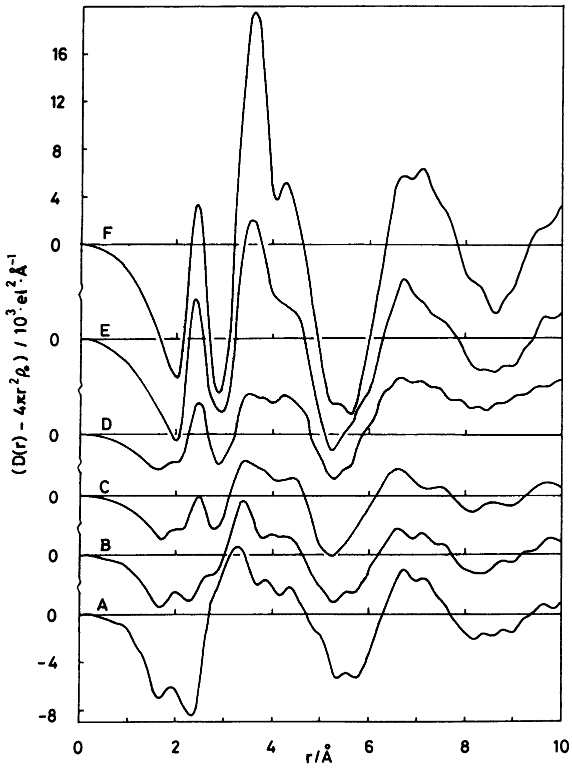

Fig. 2. $D(r)-4\pi r^2\rho_0$ curves for the solutions A—F.

The peak area around 2.0 Å decreases as the concentration of $CuBr_2$ increases, *i.e.*, the area becomes smaller in the order of the solutions, A>B>C>D; for the solution E the corresponding peak becomes very small and obscure; and for the solution F no peak is observed in this region. It has already been established that the hexaaquacopper(II) complex existing in the aqueous 3.550 mol dm^{-3} $Cu(ClO_4)_2$ solution holds a distorted octahedral form wherein the central Cu^{2+} ion binds four H_2O molecules at the equatorial sites with a distance of 1.94 Å and two H_2O molecules at the axial sites with a distance of 2.43 Å.[16] Thus, the above peak around 2.0 Å observed for the present $CuBr_2$ solutions may tentatively be ascribed to the $Cu-OH_2$ interaction at the equatorial position.

In contrast with the peak around 2.0 Å, the peak around 2.5 Å increases its peak area in the above mentioned order of solutions. The addition of the HBr causes the appearance of a quite distinct peak, as seen for the solutions E and F. In the crystal $CuBr_2$ the equatorial Cu–Br bond distance is 2.40 Å and the axial one, 3.18 Å.[11] Hence, the peak around 2.5 Å could be attributed to the interaction of the equatorial Cu–Br bond.

The broad peak located between 3.3—3.5 Å for the solutions A—D could be interpreted as being composed of the peaks due to the interaction between Br^- and OH_2 (both are free)[17] and those between Br^- and OH_2, and H_2O and OH_2 (these are bound at the *cis*-positions in an octahedral complex). An analogous peak due to these interactions was observed in the $D(r)$ curve of the highly concentrated aqueous $NiBr_2$ solution which contained predominantly $[NiBr(H_2O)_5]^+$ species.[12] In the cases of the solutions E and F that have HBr added, the comparable peak is seen at 3.6 Å, somewhat longer than 3.3—3.5 Å of the solutions A—D; this agrees with the expectation that the increased concentration of the Br^- ion aids the formation of the higher-order bromo-complexes, whereby the Br^-–Br^- interaction at the *cis*-position becomes prominent.

Then, in order to draw the structure of the predominant solute complex, the four possible geometries depicted in Fig. 3 were assumed: these are elongated octahedron (a), square pyramid (b), square plane (c), and tetrahedron (d). And the theoretical intensities $i(s)_{calcd}$ were calculated from Eq. 2, by substituting a set of the parameter values, n, r, and b that were tentatively taken for each of the assumptive models. The parameter n, the frequency factor which represents the number of the interactions between Cu^{2+} and any atom being on the axial position, was fixed at 2.0 with regard to model (a) and at 1.0 to model (b). The further refinements of these parameters were made by a least-squares method so that these gave an $s \cdot i(s)_{calcd}$ curve which was in good agreement with the observed $s \cdot i(s)$ curve in the region above $s>4$.

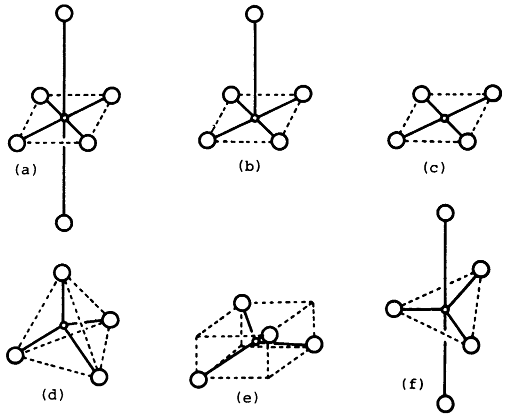

Fig. 3. Assumptive skeletal models.

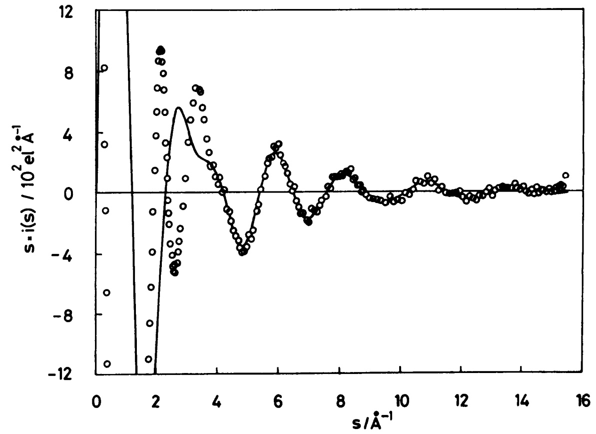

Fig. 4. Observed (○○) and calculated (——) $s \cdot i(s)$ curves for solution D.

Thus, the results indicated that the predominant complex species which existed in the solutions A—D can be most satisfactorily depicted by model (a). The

TABLE 2. REFINED PARAMETERS OBTAINED FROM THE REDUCED INTENSITY CURVE

Parameter		Solution					
		A	B	C	D	E	F
$Cu-O_{eq}$	r/Å	1.96	1.99	1.96	1.97	1.93[a]	—
	n	3.67	3.32	2.73	2.52	1.10[a]	—
$Cu-O_{ax}$	r/Å	2.50	2.51	2.41	2.37	2.42[a]	—
	n	2	2	2	2	2[a]	—
Cu–Br	r/Å	2.42	2.43	2.44	2.46	2.42[a]	2.41[b]
	n	0.33	0.60	1.10	1.31	2.91[a]	3.85[b]
$n(Cu-O_{eq})+n(Cu-Br)$		4.00	3.92	3.83	3.83	4.01[a]	—

r, Bond distance, n, frequency factor. a) The parameters obtained when model (a) was used. b) The parameters were evaluated only from the peak of the $D(r)$ curve at 2.4 Å.

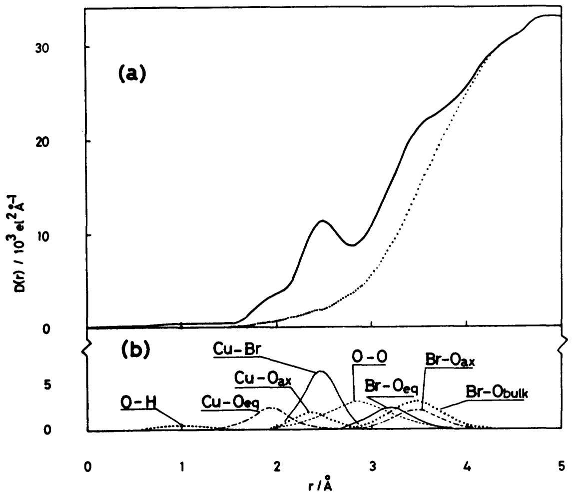

Fig. 5. (a); The $D(r)$ curve (——) and the residual distribution function (……) for solution D. The residual distribution function is obtained by subtracting the calculated peak shapes shown in (b) from the $D(r)$ curve. (b); The peak shapes calculated by using the parameter values given in Table 2.

parameter values mostly fitted by the refinements are listed in Table 2. And the $s \cdot i(s)_{\text{calcd}}$ curve calculated from these data are in good agreement with the observed $s \cdot i(s)$ curve as is exemplified in Fig. 4 for the solution D. In Fig. 5, it is shown that the residual distribution function curve obtained by the subtraction of the $s \cdot i(s)_{\text{calcd}}$ curve from the observed $s \cdot i(s)$ curve gives a smooth curve, indicating a good reliability of these parameter values. With regard to the complex in the solution E, the structure model shown in Fig. 3-(d) could be discarded, but any of the three models (a), (b), and (c) could be accepted with the same margin of uncertainty. For the complex in the solution F, none of the above four models was satisfactorily consistent with the resultant data.

Discussion

On increasing $CuBr_2$ concentration in the aqueous solution, if the coordination of the Br^- ion occurred first at the axial and then at the equatorial sites, we think that the peak in the $D(r)$ curve owing to the axial Cu–Br interaction would appear at *ca.* 3.18 Å.[11] However, Figs. 1 and 2 show no appearance of such a peak, indicating no axial coordination of Br^- in the present solute complexes. And Table 2 shows that with increasing $CuBr_2$ concentration the mean frequency factor of the equatorial Cu–Br interaction increases and that of the equatorial Cu–O decreases, while the sum of the respective value is *ca.* 4, being invariable throughout the solutions A—D with different concentrations. These facts concur with the proposed structure-model (a) of the solute complex. The equatorial Cu–Br bond distance, 2.42—2.46 Å, is more close to the equatorial Cu–Br bond distance, 2.40 Å, than to the axial Cu–Br bond distance, 3.18 Å; these are known for the crystal $CuBr_2$.[11] Moreover, the distances of equatorial Cu–O, 1.96—1.99 Å, and of axial Cu–O, 2.37—2.51 Å, of the solute complex are, respectively, comparable to those of 1.943—1.976 and of 2.399—2.448 Å of crystal $CuSO_4 \cdot 3H_2O$.[18]

As has been pointed out, the mixed-ligand complexes $[Cu(NH_3)_4(H_2O)_2]^{2+}$ and $[Cu(en)_2(H_2O)_2]^{2+}$ hold H_2O, which is a weaker ligand than NH_3 or en, at the axial site; this structure of coordination is reasonably interpreted to be more stable than that which holds H_2O at the equatorial site. Thus, only judging from the spectrochemical series, it is predicted that in the mixed-ligand aquabromocopper(II) complexes the coordination of H_2O, which is a stronger ligand than Br^-, would occur at the equatorial site rather than at the axial site. On the contrary, the solute mixed-ligand complex in the aqueous $CuBr_2$ solution seems to have H_2O at the axial site. Though this work offers no kinetic datum of the complex-formation equilibrium, this structure implies a little difference in the apparent coordination abilities of H_2O and Br^- toward Cu^{2+} ion.

No satisfactory result of the data refinements was drawn for the solutions E and F. However, the peak at 2.4 Å on the $D(r)-4\pi r^2\rho_0$ curves might be attributed to the Cu–Br interaction. And in the aqueous solution, the presence of Cu^{2+} ions binding three, five, or six Br^- ions were not evidently indicated from the electronic spectral investigations.[19] By taking these results into consideration, the minimum amounts of Cu^{2+} existing in a tetrabromo complex species in solutions E and F were tentatively calculated from the peak areas in the

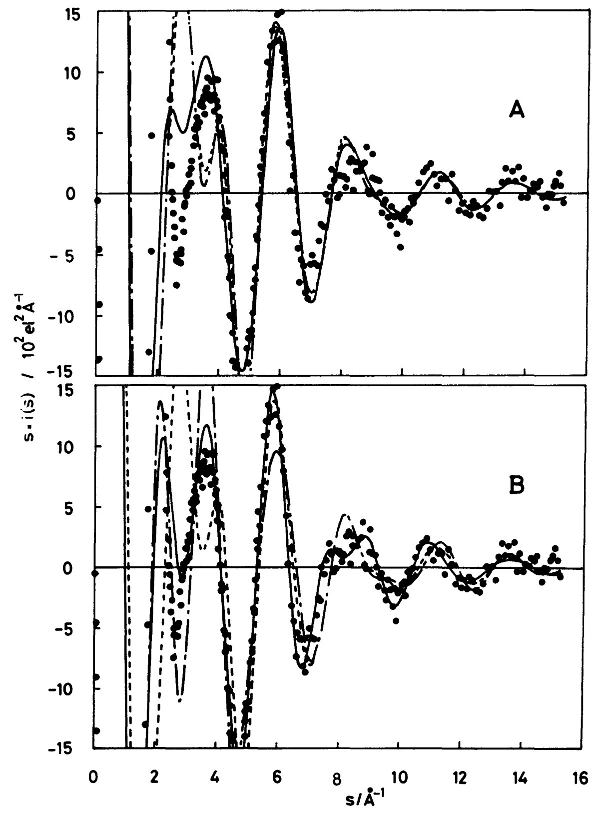

Fig. 6. Observed and calculated $s \cdot i(s)$ curves for solution F. A: Observed (●●); calculated for model (a) (— — —), for model (b) (——), for model (c) (------). B: Observed (●●), calculated for model (d) (— — —), for model (e) (——), for model (f) (------).

$D(r)$ curves: these are 92.5% of the total Cu^{2+} concentration in solution F, and 45.5% of that in solution E.[20] If the tetrabromo complex species had either a square-planar or tetrahedral structure, the Br^-–Br^- interactions within these complex molecules would give rise to the appearence of the peaks on the $D(r)$ and $D(r)-4\pi r^2\rho_0$ curves at around 3.41 and 4.82 Å for the former, or at around 3.94 Å for the latter. However, actually no peak is observed at these positions, but two peaks, a larger one at *ca.* 3.6 and a smaller one at *ca.* 4.35 Å, are observed. These facts led us to propose a flattened tetrahedral structure of the tetrabromo complex species, as shown in Fig. 3-(e). This structure is similar to that of $[CuBr_4]^{2-}$ in the Cs_2CuBr_4 crystal.[21] Then, for solution F, the observed $s \cdot i(s)$ curve is compared with the calculated ones using the refined parameter values which are taken for the assumptive models (a)—(f). In this case, a trigonal bipyramidal model (f) in Fig. 3, is also taken into consideration. As shown in Fig. 6, the curve calculated on model (e) is most like to the observed one.

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$$4 \times \frac{x}{100} + 2 \times \frac{100-x}{100} = n,$$

where n is the frequency factor of Cu–Br interaction.

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